



On the catalytic hydrogenation of polycyclic aromatic hydrocarbons into less toxic compounds by a facile recoverable catalyst

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ABSTRACT

Here we present the catalytic hydrogenation of polycyclic aromatic hydrocarbons (PAHs) to less toxic mixtures of saturated and partial unsaturated polycyclic hydrocarbons under mild reaction conditions using a magnetically recoverable rhodium catalyst and molecular hydrogen as the exclusive H source. The catalyst is easily recovered after each reaction by placing a permanent magnet on the reactor wall and it can be reused in successive runs without any significant loss of catalytic activity. As an example, anthracene was totally converted into the saturated polycyclic hydrocarbon form (ca. 60%) and the partially hydrogenated form, 1,2,3,4,5,6,7,8-octahydroanthracene (ca. 40%). The catalyst operates in a broad range of temperature and H₂ pressure in both organic and aqueous/organic solutions of anthracene and it also exhibits significant activity at low substrate concentrations (20 ppm). This can be an efficient recycling process for hydrogenation of PAHs present in contaminated fluid waste streams.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been widely acknowledged as the main toxic components of crude oil and petroleum compounds due to the high carcinogenic and mutagenic properties associated with their metabolites [1]. The PAHs are also produced in combustion processes including incomplete burning of coal, wood and other carbon-based fuels, or incineration of solid waste [2], and they can be found as pollutants in air, soil and water resources. Due to their lipophilic character (K_{ow} 10^4 to 10^7) [2], these compounds exhibit persistence in soil and tend to associate with the soil phase, especially when the soil has a substantial organic content [3]. PAHs are not significantly soluble in pure water, but the presence of dissolved or particulate organic matter provides these compounds with considerable mobility [4], which increases the harmful environmental effects of these substances.

The occurrence, distribution and potentially toxic effects of PAHs to human health have prompted researchers to address ways to detoxify these organic compounds from the natural environment and industrial sites. Bioremediation is an approach that promotes the natural attenuation of the contaminants [5], however the proposed mechanism involves the oxidation of the aromatic ring, followed by the systematic breakdown of the

compound to PAH metabolites and/or carbon dioxide. Some oxidized intermediates may have higher solubility in water than the PAH and are therefore potentially more bioavailable, and could present a greater toxicity than the PAH itself. Therefore, catalytic oxidation constitutes a less interesting pathway for the chemical treatment of such residues, unless the total oxidation of the contaminant to CO₂ is accomplished [6]. The reductive hydrogenation is considered a more convenient method to transform PAHs into less harmful compounds [7], since less toxic intermediates are formed. For example, the hydrogenated product tetralin shows higher oral rates LD₅₀ levels and faster biodegradation rate than its precursor naphthalene [7].

Many catalytic systems for reduction of PAHs can be found in the literature [7–19]. Most of them are active only at high pressures and temperatures, and therefore efforts to optimize the reaction to proceed under mild conditions are desired [16]. The development of catalysts for hydrogenation of PAHs by molecular H₂ is quite beneficial because it guarantees a clean source of H atoms, which in turn, eliminates the use of common stoichiometric non-friendly routes. A search in the current literature reveals that the attempts to perform PAHs hydrogenation in liquid phase are still commonly accomplished by means of a strong reducing agent, such as NaBH₄ [7,18,19].

Metal nanoparticles (MNPs) have attracted much attention especially in organic synthesis due to their unique catalytic activities compared to their bulk counterparts. However, studies on the performance of MNPs in hydrogenation of PAHs are still

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scarce [8,16–19]. Recently, we have reported a strategy to stabilize metal nanoparticles on magnetic oxides coated with functionalized silica [20]. Compared to previously reported results, the catalyst exhibits outstanding catalytic activity for hydrogenation of arenes and olefins under mild conditions. The inherent magnetic property allows a rapid separation of the catalyst from the reaction media and an easy catalyst recycling. Besides, it eliminates the use of any further physical or chemical product-isolation procedures. We believe this catalyst is promising for PAHs hydrogenation due to the high catalytic activity attained for benzene hydrogenation. Moreover, its easy separation, recycling and negligible metal leaching can be extremely beneficial in organic synthesis and chemical treatment of hazardous substances.

Here we report the performance of rhodium nanoparticles stabilized in silica-coated magnetite in the liquid hydrogenation of PAHs under mild conditions using H_2 as the exclusive H source.

2. Materials and instrumentation

2.1. Preparation of rhodium catalyst

The magnetically recoverable catalyst support, comprised of silica-coated magnetite nanoparticles ($Fe_3O_4@SiO_2$), was prepared following the procedure described previously [20,21]. The catalyst was prepared by adding 100 mg of amino-functionalized $Fe_3O_4@SiO_2$ to 20 mL of an aqueous rhodium chloride solution (4.2 mg). The mixture was stirred for two hours at 25 °C. The solid was then magnetically collected from the solution and washed twice with acetone followed by drying at 100 °C for 2–3 h. The metal-loaded solid was dispersed in cyclohexene (2 mL) and submitted to molecular hydrogen (6 atm) at 75 °C for ca. 20 min. The reduction of the metal ions and formation of Rh(0) nanoparticles on the solid support were monitored by the H_2 consumption in the concomitant reaction of hydrogenation of cyclohexene. The Rh content in the final solid was analyzed by ICP OES: 1.5 wt%.

2.2. Hydrogenation experiments

The catalytic reactions were carried out in a modified Fischer–Porter glass reactor connected to a pressurized hydrogen tank at 20–50 atm. The Fischer–Porter bottle was set at a constant pressure for the entire course of the reaction by leaving it open to the hydrogen supply. In a typical experiment, catalytic quantities of rhodium (5 mg of magnetic solid), the desired quantity of substrate and cyclohexene as solvent were added to the reactor under inert atmosphere. The reactor was evacuated and attached to the hydrogenation apparatus. The reaction was conducted under magnetic stirring (700 rpm) at the desired pressure and temperature. The temperature was maintained constant by a hot-stirring plate connected to a digital temperature controller. After the desired time, the catalyst was recovered magnetically by placing a magnet on the reactor wall and the products were collected and analyzed by gas chromatography (GC) and GC–MS. For the experiments carried out in different pressures and temperatures, the reaction time was set to 15 min and the reaction rate was monitored spectrophotometrically by measuring the characteristic absorbance band of anthracene at 376 nm.

2.3. Characterization methods

Gas chromatography analyses were performed on a Shimadzu GC 17A, equipped with a 30 meter capillary column with a dimethylpolysiloxane stationary phase, using the following parameters: initial temperature: 40 °C, initial time: 5 min, ramp: 10 °C min⁻¹, final temperature: 250 °C, final time: 5 min, injector and detector temperature: 250 °C, injection volume: 2 μ L.

UV–vis analyses were performed in a Shimadzu UV 1700 spectrophotometer using a quartz cuvet with 1 cm optical pathway.

TEM analyses were performed on a Philips CM 200 operating at accelerating voltage of 200 kV. The samples for TEM were prepared by collecting the nanoparticles dispersed in aqueous solution on a carbon-coated copper grid.

The X-ray photoelectron spectra were obtained with a VSW HA-100 spherical analyzer using an aluminum anode (AlK α line, $h\nu = 1486.6$ eV) X-ray source. The high-resolution spectra were measured with constant analyzer pass energies of 44 eV, which produce a full width at half-maximum (fwhm) line width of 1.7 eV for the Au(4f7/2) line. The powdered samples were pressed into pellets and fixed to a stainless steel sample holder with double-faced tape and analyzed without further preparation. To correct for charging effects the spectra were shifted so that the C 1s binding energy was 284.6 eV. Curve fitting was performed using Gaussian line shapes, and Shirley type background was subtracted from the data.

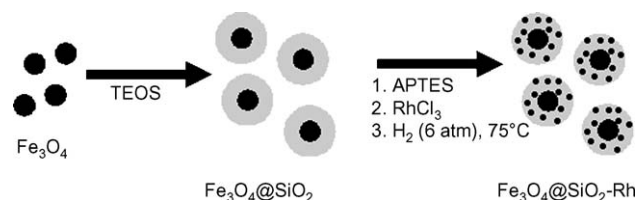
3. Results and discussion

The magnetically recoverable Rh catalyst used in this study was obtained as reported previously [20]. The preparation of the catalyst follows the steps depicted in Scheme 1.

The catalyst exhibits magnetic properties due to the presence of superparamagnetic Fe_3O_4 nanoparticles, which were spherically coated with silica by means of a reverse microemulsion so as to be used as catalyst support. The magnetic silica spheres ($Fe_3O_4@SiO_2$) were functionalized with the silane coupling reagent 3-(amino-propyl)-triethoxysilane (APTES) to give amino-modified silica surfaces, which were used to immobilize the metal precursor. The solid could be easily loaded with metal ions when stirred with aqueous rhodium chloride and readily recovered by applying a magnetic field. The Rh^{3+} loaded solid was dispersed in cyclohexene and submitted to molecular hydrogen for metal reduction under mild conditions (6 atm H_2 , 75 °C), to give well dispersed Rh(0) nanoparticles deposited on the solid surface. The formation of the Rh(0) nanoparticles was followed by the concomitant reduction of cyclohexene, which serves as the reporter reaction for the metal nanoparticles formation. The catalyst preparation was optimized in such a way so that it always contains ca. 1.4–1.6 wt% of Rh, as determined by atomic absorption analysis (ICP OES). The solid dubbed $Fe_3O_4@SiO_2$ -Rh(0) was previously characterized by TEM and EDS analysis.

Fig. 1 shows a representative TEM image showing the spherical morphology of the catalyst support and the presence of the 3–5 nm Rh(0) nanoparticles on the surface after metal immobilization and reduction.

Here we also complete the catalyst characterization by XPS analysis. The supported rhodium nanoparticles were analyzed by X-ray photoelectron spectroscopy to examine the oxidation state and the chemical environment of the deposited metal. Fig. 2 shows the photoemission spectrum of the Rh 3d core level. Two contributions corresponding to different rhodium species can be observed after deconvolution of the Rh 3d spectrum (Fig. 2). The



Scheme 1. Preparation of the Rh(0) catalyst.

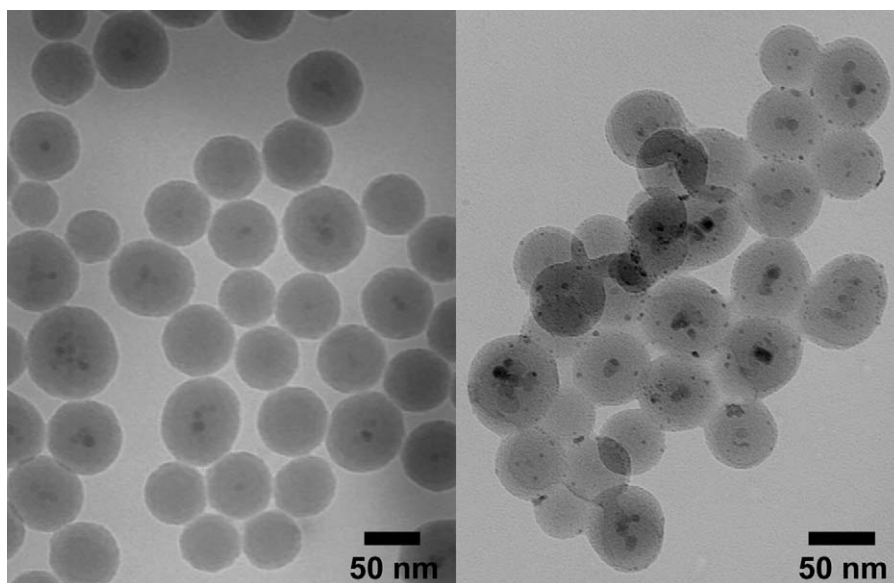


Fig. 1. Transmission electron microscopy of the catalyst support (left) and the Rh(0) magnetically recoverable catalyst (right).

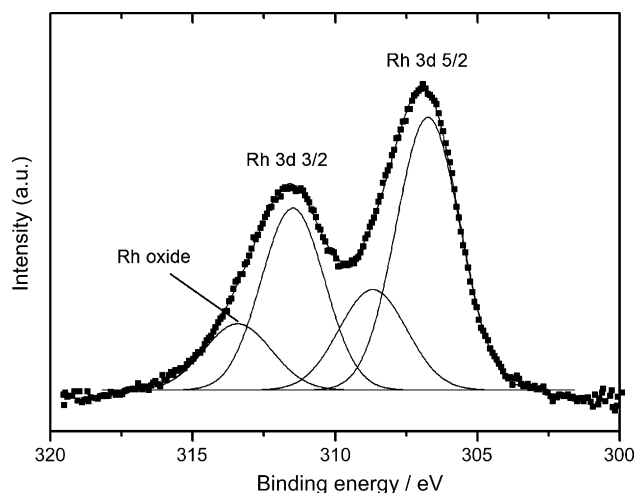


Fig. 2. Deconvolution of the Rh 3d photoemission line of the Rh(0) magnetically recoverable catalyst.

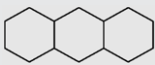
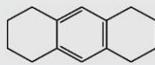
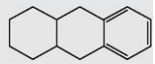
low binding energy signal (BE of 3d_{3/2} at 311.5 eV and 3d_{5/2} at 306.8 eV) is consistent with rhodium metal whereas the higher (BE of 3d_{3/2} at 313.4 eV and 3d_{5/2} at 308.7 eV) agrees with the presence of oxidic rhodium species. The presence of oxygen O 1s peak binding energy at 530.3 eV, characteristic of lattice oxide, and the coincidence with the binding energy upshift of the Rh(3d) peak suggests surface oxidation. This partial oxidation probably

occurred during the sample preparation. Also, peaks associated with N 1s and C 1s relative to the APTES ligand used to functionalize the silica surface were present, and the Si 2p and O 1s corresponding to the silica support were found, respectively, at 103.5 and 532.7 eV [22–24]. Absence of the Cl signal indicates that the surface is not contaminated by Cl[−] from the metal precursor.

Preliminary studies on the activity of the supported Rh catalyst have shown very interesting results on the hydrogenation of aromatics. Benzene was converted to the totally hydrogenated alkane with TOF of 1100 h^{−1} and total TON of 11550 mol substrate per mol catalyst after 20 successive runs at 75 °C and 6 atm of H₂ [20]. Our research is now directed to the performance of the catalyst in the hydrogenation of polycyclic aromatic hydrocarbons. The catalytic hydrogenation of anthracene was examined as a model reaction. Three main products have been reported in the hydrogenation of anthracene, corresponding to the hydrogenation of the central ring, the two side rings, or only one side ring, and the total hydrogenated form to the alkane is rarely accomplished [25].

The catalytic reactions were carried out in mild conditions in a modified Fischer–Porter glass reactor connected to a pressurized hydrogen gas tank. The Fischer–Porter bottle was set at a constant pressure (6 atm) for the entire course of the reaction by leaving it open to the hydrogen supply. After the desired reaction time the catalyst was recovered magnetically and the products analyzed by GC–MS. The conditions used, and the conversion and selectivity achieved in the hydrogenation of anthracene using the Rh(0) catalyst are summarized in Table 1.

Table 1
Hydrogenation of anthracene by Rh(0) magnetically recoverable catalyst.

Products (%)			
Reaction 1 ^a	59.7%	39.5%	ND ^d
Reaction 2 ^b	ND	84.8%	15.2%
Reaction 3 ^c	ND	81.4%	18.6%

Reaction conditions: 1 mL cyclohexane, 5 mg Rh catalyst 1.5 wt% (0.0007 mmol Rh), *t* = 24 h, *T* = 75 °C, P_{H₂} = 6 atm.

^a Substrate: 0.34 mg (0.0019 mmol).

^b Substrate: 1.70 mg (0.010 mmol).

^c Recycling the catalyst of reaction 2.

^d Other partially hydrogenated forms = 0.8%. ND = not detected.

Our supported Rh(0) nanoparticles were able to catalyze the total conversion (>99%) of the substrate into the hydrogenated counterparts under mild reaction conditions. On top of that, 59.7% of the products obtained correspond to the completely hydrogenated form when higher catalyst to substrate molar ratio was used (Table 1 – reaction 1). This result is very expressive compared to those previously reported; where even with the use of strong substances as hydrogen donor, like for example sodium borohydride, only partially hydrogenated products were usually attained. It is worth mentioning that no conversion of anthracene was detected with the commercial Rh/C (5 wt% of Rh) catalyst after 2 h of reaction at 25 °C with 10 atm of H₂ [25]. Lower catalyst to substrate molar ratio (Table 1 – reaction 2) changed the distribution of species in the products, and the totally hydrogenated form was not detected. Further experiments were performed to verify the catalyst stability and recyclability. After a first run (Table 1 – reaction 2), the magnetically recovered catalyst was reused for a second run by addition of a new portion of anthracene. The catalyst showed similar activity (Table 1 – reaction 3) with complete conversion of anthracene to the same partial hydrogenated products. No leaching of metal to the organic phase was noticed, as the Rh content in the products after recovering the catalyst exclusively by magnetic separation was <0.01 ppm (ICP OES analysis). The organic phase is also free of Fe and Si, which corroborates the high stability of our catalyst.

In order to evaluate the effect of the hydrogen pressure in the anthracene hydrogenation, several reactions were performed at different H₂ pressure conditions. The anthracene conversion was measured after 15 min of reaction by the decrease of its characteristic absorption at 376 nm (initial concentration 20 ppm) upon hydrogenation. The fall of the anthracene peak was followed by the appearance of other peaks at higher energies. Moreover the less intense the anthracene peak became, the higher was the absorbance of those forthcoming peaks. This is a direct consequence of the formation of partially hydrogenated products that, as expected, absorb at lower wavelengths. That is a strong evidence that even in low concentrations of substrate a reaction is taking place rather than a mere physisorption of anthracene. Besides when submitted to the same reaction conditions used in the hydrogenation experiments, the Fe₃O₄@SiO₂ support itself did not show any change in the UV–vis spectrum of anthracene. As shown in Fig. 3, the substrate conversion at 50 °C is highly dependant on the hydrogen pressure as it varies from 1 to 6 atm. Increasing the hydrogen pressure causes an increase on the

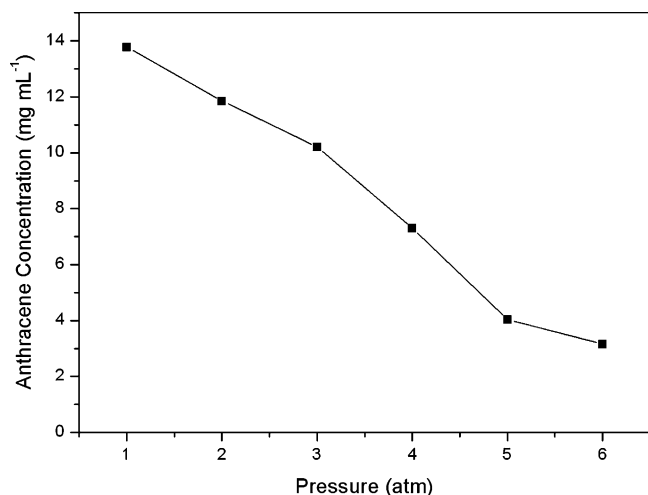


Fig. 3. Hydrogenation of anthracene as a function of pressure of H₂. Reaction conditions: 5 mL of a 15 mg L⁻¹ anthracene–cyclohexane solution, 5 mg of catalyst (1.5 wt% Rh), T = 50 °C.

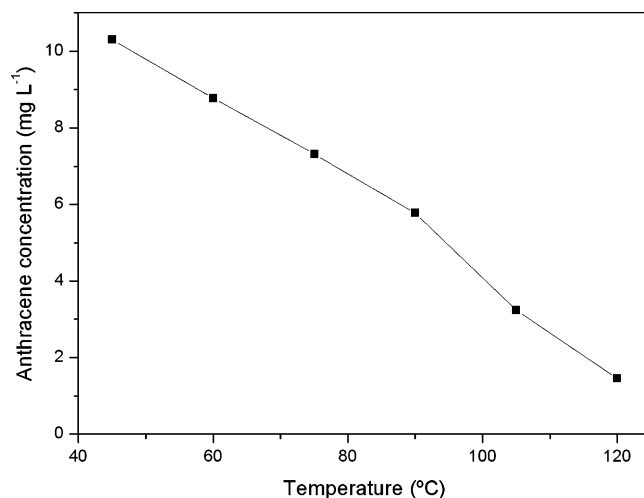


Fig. 4. Hydrogenation of anthracene as a function of temperature. Reaction conditions: 5 mL of a 15 mg L⁻¹ anthracene–cyclohexane solution, 5 mg of catalyst (1.5 wt% Rh), pressure of H₂ = 3 atm.

substrate conversion from 8% (at 1 atm) to 73% (at 5 atm), however a less pronounced effect was observed above 5 atm. This can suggest that at hydrogen pressure <5 atm the reaction is under mass transfer controlled processes. Under these circumstances, the catalyst seems to be able to promote the PAHs hydrogenation to some extent even at pressure as low as 1 atm, which allows the solid to be used in ultra-mild condition reactions.

We were also interested in studying the effect of the temperature on the hydrogenation reaction. Therefore, several hydrogenation reactions were performed varying the temperature from 45 to 120 °C. As shown in Fig. 4, the substrate conversion after 15 min of reaction is highly dependant on the temperature, and higher conversions were obtained at higher temperatures. Varying the temperature can influence many reaction parameters (energy barriers, mass-transfer limitations, solubility, etc.) that could affect directly the global reaction and contribute for the rather linear profile obtained. In hydrogenation reaction, one can expected that upon increasing the temperature the expulsion of the dissolved hydrogen occurs, leading to a complex kinetic profile and eventually to a decrease on global reaction rates.

Overall, the hydrogenation activity displayed by the catalyst in such a low substrate concentration of anthracene (20 ppm) is quite interesting as only traces of PAHs are usually found in the environment, so a catalyst that is active under such conditions is very desired. Notably, the catalyst is also tolerant to water. The presence of 20 wt% of water in the reaction media does not deactivate the catalyst. This is noteworthy for practical applications, specifically the treatment of wastewater containing PAHs vestiges.

4. Conclusions

In summary, our highly stable magnetically recoverable catalyst formed by Rh nanoparticles well distributed and stabilized on the magnetic support surfaces has shown very interesting catalytic activities in the liquid hydrogenation of PAHs. The important features provided by the catalyst are: (i) absence of Rh, Fe and Si detachment into the products; (ii) easy catalyst recovery by simply applying an external magnetic field; (iii) activity under mild reaction conditions, which is quite novel for hydrogenation of PAHs as properly referred in the introduction; (iv) activity in a broad range of temperatures and pressures; (v) possibility of reusing the catalyst in successive reactions; (vi) use of molecular hydrogen as the exclusive “clean” H source, while most previous

work use environmentally unfriendly reducing agents; (vii) selectivity to the complete hydrogenated form of anthracene (tetradecahydroanthracene), which has rarely been achieved, and it is important in detoxification processes since the more the number of π bonds in the molecule the more carcinogenic it is and (viii) activity in low PAHs concentration (as low as 20 ppm), which makes the use of this catalyst quite interesting as PAHs are found in the environment in relative low concentrations. Thus, the properties exhibited by the catalyst can give rise to an efficient green recycling process for hydrogenation of PAHs present in contaminated fluid waste streams.

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